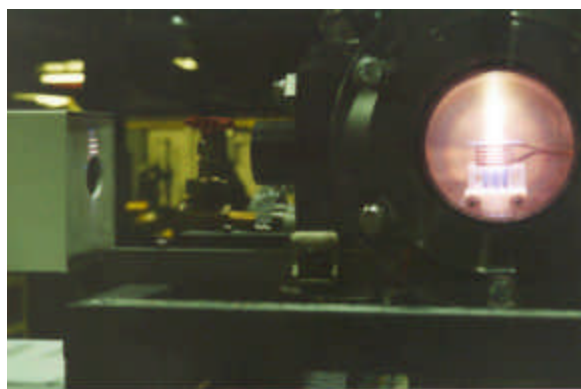


Testing of a Continuous Sampling Air-ICP System as a Continuous Emission Monitor at the Diagnostic Instrumentation and Analysis Laboratory

September 12-17, 1999

David P. Baldwin, Daniel S. Zamzow, and David E. Eckels, Ames Laboratory,
and George P. Miller, Robin Wiser, and Shiquan Tao, DIAL

Ames Laboratory-USDOE
Report IS-5138
October 5, 1999



1. Introduction

This report has been prepared to document the performance of the reduced-pressure air-ICP-AES (inductively coupled plasma – atomic emission spectroscopy) system developed by Ames Laboratory for use as a continuous emission monitor (CEM). This work was funded by the U. S. Department of Energy, Office of Environmental Management, Office of Science and Technology, through the Characterization, Monitoring and Sensor Technology Cross-cutting Program (CMST-CP). The purpose of the project is to develop spectroscopic tools and methods for spectroscopic field monitoring techniques. During FY99 this has included the development of this new plasma emission and sampling system, as well as the continued development of the AOTF-echelle spectrometer, a compact, high-resolution, solid-state detection system that has potential use in a wide range of emission- and absorption-based techniques.^{1,2} The first task for this project in FY99 was the development of multi-wavelength simultaneous capabilities for the AOTF-echelle spectrometer. This milestone was completed during the summer of FY99. The second task was the assembly of the reduced-pressure air-ICP and sampling system, and the testing of this system at Mississippi State University with our collaborators at the Diagnostic Instrumentation and Analysis Laboratory (DIAL). That task was completed in September 1999. This report is the deliverable associated with that task. In this report we describe the reduced-pressure air-ICP and continuous sampling system, the characteristics and performance of these systems, and the results of the field test performed at DIAL.

The reduced-pressure air-ICP CEM is being developed in response to the need of DOE and other organizations to monitor the heavy-metal or radioactive materials that may be released during the processing or combustion of hazardous or mixed-waste materials. The promulgation of regulations limiting the release of these materials and requiring continuous monitoring of the stack gases from these processes would seriously impact the operations of DOE waste incinerators and other facilities. Therefore, it is important to develop and validate techniques that adequately meet proposed sensitivity and accuracy requirements. The most likely form of validation for such a technique will involve comparison of CEM results for a test combustion system with EPA Reference Method 29 (RM-29).³ Therefore, the air-ICP CEM developed during this project was tested at DIAL by monitoring metal emissions in a fuel oil-air combustion exhaust while simultaneously collecting samples using the RM-29 technique. The CEM results were available continuously during the on-line monitoring that was performed. However, the results of the RM-29 sampling are not complete at this time, but will be appended to this report with a comparison and evaluation when they are available.

This CEM system was first assembled at Ames Laboratory and tested with an ICP power supply and matching network in the laboratory. This report contains some results for sensitivity and stability tests obtained in the laboratory. The test at DIAL was planned to involve a number of tasks including: 1) integration of a compact solid-state ICP power supply and its matching network with the reduced-pressure plasma system developed at Ames; 2) integration of the AOTF-echelle spectrometer developed at Ames and delivered to DIAL in FY98 (this is a single-wavelength, rapid-sequential spectrometer) with the reduced-pressure air-ICP system; 3) connection of the reduced-pressure air-ICP and continuous sampling system to a sampling port on the DIAL “test stand” (combustion system); and 4) operation of the CEM for metals analysis while simultaneously collecting samples using RM-29 for later comparison. The testing done at DIAL was the first field test of the continuous sampling air-ICP system developed at Ames during FY99. While a number of issues arose during this test, as expected during any first-time experimental field effort, all of these tasks were accomplished, and an understanding of a number of significant issues was obtained. Armed with this understanding, we can describe the successful outcome of this test and describe our plans for improvements in the instrumentation and methods.

The application of various plasma and electrical discharge sources for monitoring the elemental composition of aerosols, vapors, and airborne contaminants has a long history.⁴ The energy available in a plasma source such as an ICP is sufficient to vaporize and atomize all but the largest airborne particles and to excite these atoms to optically bright atomic and ionic states. The resulting optical emission is sufficiently intense and characteristic to identify and quantify all but a handful of the elements at trace levels.^{5,6} The ICP is a uniquely useful source for these types of measurements due to its extremely high temperature, simplified operation at atmospheric and near atmospheric pressures, and relative insensitivity to changes in the sample matrix.

There are, however, a number of obstacles to the implementation of ICP – atomic emission spectroscopy (ICP-AES) for field applications, such as stack-gas monitoring and air monitoring. First, the standard laboratory-

based ICP operates using argon for the plasma discharge gas as well as the gas carrying vapors, aerosols, or particles to the plasma. The use of argon necessitates a continuous supply of argon from cylinders or a dewar, either of which limit the mobility and untended operation of an ICP. Additionally, the argon ICP is somewhat sensitive to the addition of air, especially moist air, as the carrier gas for the sample material. One way to overcome these difficulties is to use air from a compressor as the plasma gas in the ICP. An air-ICP requires a larger power supply and an air compressor for operation, but requires only a small amount of argon when the plasma is ignited, requires no additional gas cylinders for continuous operation, and is easily operated with air or nitrogen as the sample or carrier gas. These characteristics make air-ICP-AES an excellent source for air and stack-gas monitoring.⁷⁻⁹ The details of operation of the air-ICP have been described elsewhere.^{7,9} Previous work using the air-ICP as a source for emissions monitoring has utilized an atmospheric-pressure plasma. Samples from the stack gas or air are drawn to fill a sampling loop, and valves are then switched and compressed air is used to force the sampled gases from the loop into the plasma. In this way, gas can be drawn isokinetically from a stack at high flow rates and injected at the lower flow rates needed for operation of the ICP.^{10,11} This method has some problems including a duty cycle that limits the exposure times for the optical measurement to a few seconds, additional lost time during equilibration of the plasma, and the potential for drop out of particles at the slower velocity used for sample injection. For these reasons, we have developed a system that uses continuous sampling into a reduced-pressure ICP. Other work has used reduced-pressure plasmas to draw the sample gas directly into the plasma with no injection loop.¹² That system used a non-standard ICP torch, with the sample gas providing the entire plasma gas flow. This arrangement suffers from a number of limitations associated with self-absorption of the analyte emission lines at the cold boundaries of the plasma. This is the reason that standard analytical ICP torches have three concentric gas channels, with the analyte confined in the center of the plasma. Our work uses a standard three-channel ICP torch. For our reduced-pressure air-ICP system, gas is sampled isokinetically into an intermediate chamber. Gas from the intermediate chamber is isokinetically sampled again and is drawn into the plasma by the reduced pressure in the plasma chamber. This system allows for continuous sample introduction with no dead time for loading a sample loop and waiting for the plasma to equilibrate to the sample during an injection cycle. The design of this continuous sampling air-ICP system and its operation during testing at DIAL are discussed in this report.

2. Experimental

A laboratory photograph of the continuous sampling air-ICP system at Ames Laboratory (AL) is shown in Figure 1. The system consists of an air-ICP that is operated at reduced pressure inside a 6"-diameter metal enclosure, a Teflon sampling chamber, and an acousto-optic tunable filter (AOTF) – echelle spectrometer system that is used to detect ICP optical emission signals resulting from metals introduced into the plasma. The Roots blower, sampling pump, and ICP generator that are required for operation of the system are not shown in the photograph.

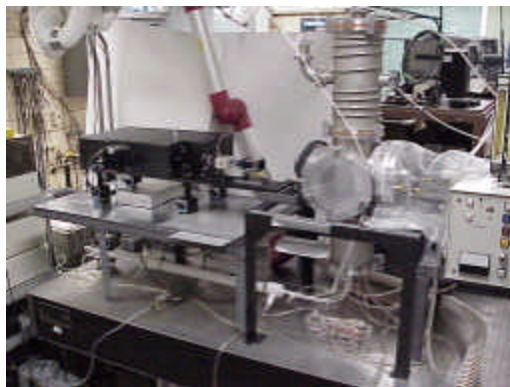


Figure 1. Photograph of the continuous sampling air-ICP system, including the ICP metal enclosure, part of the ICP automatching network (on the right side), the Ames AOTF-echelle spectrometer (mounted on the angle-iron stand, on the left side), and the Teflon sampling chamber (below the stand, shown without the heat-tracing and insulation described in the text).

2.1. Enclosed ICP System

A schematic diagram of the enclosed ICP system and a photograph of the ICP torch, showing the connections to the automatching network of the ICP generator system at AL, are shown in Figure 2 (a) and (b)

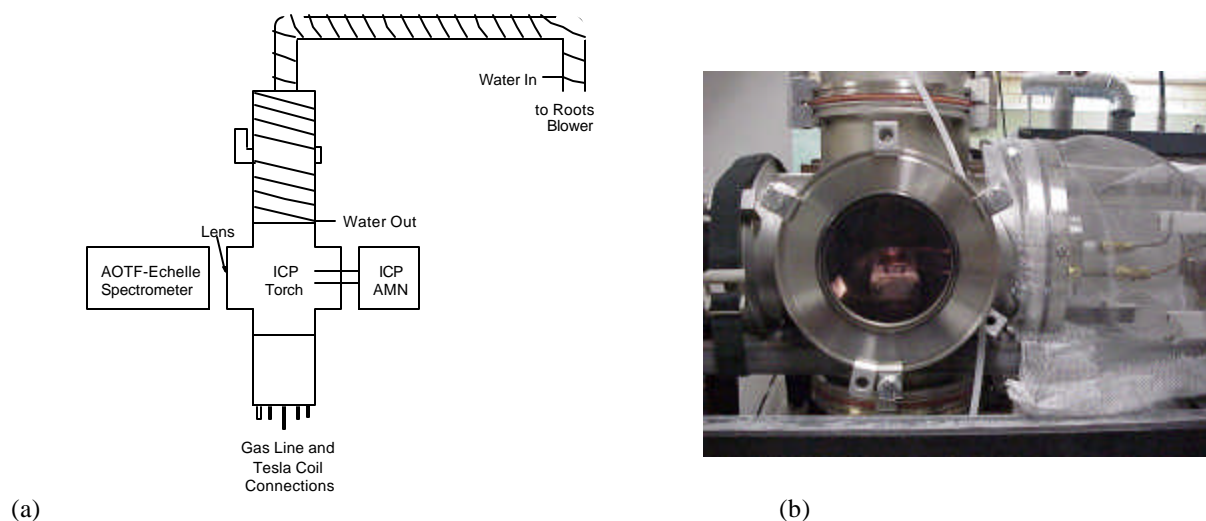


Figure 2. (a) Schematic diagram of the enclosed ICP system and (b) photograph of the ICP torch inside the 6"-diameter metal enclosure, showing the RF connections to the automatching network (AMN) of the ICP generator system.

The metal enclosure that is currently being used for the continuous sampling air-ICP system was originally developed for continuous monitoring of alkali metals in coal and biomass combustion and in gasification process lines, by flame emission spectroscopy. The system has been modified for ICP operation by making provisions for mounting the ICP torch inside the 6"-diameter stainless steel 6-way cross and providing the required ICP gas line, Tesla coil, and AMN connections. The metal enclosure is comprised of standard 6"-diameter (ISO 160) stainless steel vacuum components (Huntington Labs and MDC Vacuum Products Corporation). The bottom flange of the enclosure has gas-line connections for the ICP torch plasma and auxiliary gas supplies and for the ICP axial channel (sample) gas, which is connected to the Teflon sampling chamber. A connection point for the Tesla coil discharge required to ignite the ICP is included on the bottom flange of the enclosure. An additional gas-line connection on the bottom flange is provided for the introduction of supplemental air (60-80 L/min), which provides some cooling of the metal enclosure during operation of the 3-kW air plasma. The supplemental air passes through a glass sparging tube (Thomas Scientific) inside the metal enclosure to disperse the air throughout the bottom of the enclosure. Above the ICP torch, 1/4"-diameter stainless steel tubing is welded onto the 6"-diameter metal enclosure, for water-cooling of the upper portion of the enclosure. At the top of the enclosure, 1.5"-diameter stainless steel tubing (also water-cooled) is connected. The Roots blower (assembled by Grubb Equipment Corporation, St. Paul, MN) is connected to this 1.5"-diameter tubing to operate the enclosure at reduced pressure, 0 to -5 psig, in order to draw sample continuously into the plasma, from the sampling chamber, through the axial channel of the ICP torch. Optical emission signals from metals introduced into the air-ICP are detected using the AOTF-echelle spectrometer. A 2"-diameter, 3" focal-length fused silica lens, mounted in the flange on the 6-way cross between the air-ICP and the spectrometer, forms a 1:1 image of the plasma at the input aperture of the AOTF-echelle spectrometer

The AMN of the ICP generator system is connected to the load coil of the ICP torch by copper tubing that passes through a 6"-diameter (ISO 160) bolt flange, on the right side of the 6-way cross, as shown in Figure 2(b). (The AMN is cut-off on the right side of the photograph.) The high-voltage RF electrode is a length of 1/4"-diameter copper tubing that passes through the center of a 1/4"-diameter Teflon Swagelok bulkhead union feed-through that is mounted in the center of a Delrin flange (identical to an MDC ISO 63 stainless steel clamp flange) on the right side of the 6-way cross. The Teflon and Delrin isolate the RF voltage from the grounded stainless steel flange, thereby preventing arcing from occurring at the point where the RF electrode passes through the flange. The ground electrode is a length of 1/4" copper tubing that passes directly through the stainless steel flange. Swagelok reducing unions are used to connect the two electrodes to 1/8"-diameter copper tubing, for connection to the AMN

and to the ICP load coil. The load coil and connecting copper tubing are cooled by water flowing through the tubing, as is typical for ICP systems. With the current arrangement, no RF arcing has occurred at the interface between the AMN and the metal enclosure. Initially, a commercial ceramic RF feed-through was used. However, this feed-through failed due to arcing within the connector or to mechanical failure (breakage) of the ceramic, and was replaced with the current arrangement. As shown in Figure 2(b), grounded steel mesh, bolted to the chamber and AMN, is used to shield the operator from high RF fields and prevent incidental contact with high voltage components.

2.2. Teflon Sampling System

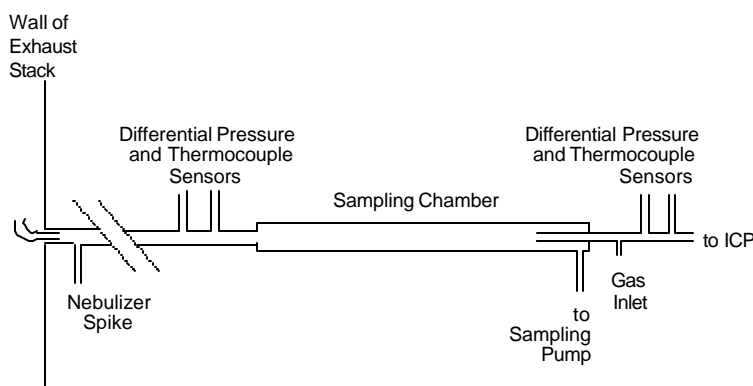


Figure 3. Schematic diagram of the Teflon sampling system, with connection to an exhaust stack.

The sampling arrangement for the air-ICP system consists of a dual-stage sampling technique. A diagram of the system is shown in Figure 3. The dual-stage system starts with a glass-lined sampling probe that extracts a gas stream from the stack. A port consisting of a Teflon tee is provided so that metal aerosols generated using a pneumatic or ultrasonic nebulizer can be introduced into the sample gas stream, in order to perform on-line calibration of the air-ICP system. The gas flows through a Teflon tube to the inlet of the sampling chamber. There are two ports (Teflon tees) that are provided for connecting a differential pressure transducer and a thermocouple, so that the gas flow rate and temperature at the inlet to the sampling chamber can be monitored. The outlet end of the chamber consists of a Teflon sampling tube and exhaust line. There are two ports provided for connecting a second set of differential pressure and thermocouple sensors, so that the gas flow rate and temperature at the outlet of this chamber (the inlet to the axial channel of the ICP torch) can be monitored. An additional port is provided as a gas inlet for argon that is used only during start-up of the plasma.

A high-volume primary sample is drawn isokinetically from a process pipe using a standard commercial EPA isokinetic glass-lined probe with an integral heater (Apex Instruments). The nozzle on the probe is a standard source-sampling nozzle with a 1/2"-inner diameter; the glass liner of the nozzle has a 5/8"-outer diameter. The outlet of the glass liner connects through an adapter to a 1/2" Teflon Swagelok tee. The side port of this tee is used for injection of calibration aerosol into the sample stream (nebulizer spike in Figure 3). The in-line port of this tee is connected to a commercial heat-traced Teflon line (Technical Heaters) that is 1/2"-outer diameter and 12' in length (not shown in Figure 3). The outlet of the heat-traced line is connected to a Teflon differential pressure flow cell. The flow element consists of a 1/4"-inner diameter tube that is 2" long. A Teflon-coated thermocouple (Omega Engineering) is inserted into the inlet of the flow cell to monitor the gas stream's temperature. The differential pressure is monitored using a differential pressure transducer (Validyne, model P55D), which has a maximum range of 3.5" of water. The outlet of the primary flow cell is connected to the inlet of the sampling chamber, which is a Teflon tube that is 1"-inner diameter and 24" in length. A lubricated vane pump (Gast Manufacturing, model 0523-V4-G180DX) draws the sample through the sampling chamber in a laminar-flow arrangement, with over 95% of the sample being removed through an exit port and exhaust line at the end of the chamber.

A secondary sample is drawn isokinetically from the gas flowing through the sampling chamber using a 1/4"-outer diameter Teflon sampling tube that is inserted approximately 4" into the end of the chamber. The tube currently used has a 0.170"-inner diameter, with a 30° taper at the sampling end. This tube can easily be exchanged for a tube with a different inner diameter to accommodate different sample velocities in the exhaust stack and still

allow appropriate sample flow into the ICP torch. The secondary sample outlet is connected to a 1/4" Teflon Swagelok tee. The in-line port of this tee is followed by another Teflon differential pressure flow cell, to monitor the sample flow rate into the reduced-pressure air-ICP. The flow element in this cell consists of a 0.094"-inner diameter Teflon tube that is 1.25" long. A second Teflon-coated thermocouple is inserted into the inlet of this flow cell. The differential pressure is monitored using an oil-filled manometer (Dwyer Instrument, model 101) that has a maximum range of 0.5" of water. The primary flow cell, Teflon sampling chamber, and secondary flow cell are heat-traced using electrical heat tape and insulation wrap. The sample flow from the outlet of the secondary flow cell passes through the bottom of the reduced-pressure chamber (metal enclosure) and into the axial channel of the ICP torch. The pressure in the chamber is reduced slightly below atmospheric pressure, to draw an appropriate sample flow, approximately 1 L/min, into the axial channel of the torch. The chamber is evacuated using a Roots-type pump (Roots Division, Dresser Industries, universal RAI model 22) that has a 1 horsepower variable speed motor.

2.3. Reduced-Pressure Air-ICP Operation

For laboratory testing performed at AL, the continuous sampling air-ICP system was operated using a Plasma-Therm model HFL5000D, 40 MHz, 5-kW ICP system. A low-flow quartz ICP torch (Precision Glassblowing of Colorado) is used, to allow operation using air or argon as the plasma gas. This torch has a reduced outer annulus width (0.5 mm) compared to a standard ICP torch (1 mm). Operation of the ICP is initiated using argon as the plasma gas, with argon introduced into the gas inlet (shown in Figure 3). The Roots blower is set to a relatively low speed (approximately 440 rpm) and the sampling pump is turned off during ICP start-up. After initiation of the argon plasma, the Roots blower speed is increased, so that argon and some air (drawn through the Teflon sampling chamber, which is open to room air on the inlet end) are introduced into the axial channel of the ICP. The RF power is increased from 1-kW to approximately 1.5-kW to sustain this argon-air plasma. At this point, the argon supply to the ICP torch plasma and auxiliary gas flows and to the gas inlet is gradually switched to air, and the RF power is increased from 1.5-kW to approximately 3-kW, as the argon plasma switches to an air plasma. After the switchover to air is complete, the plasma and auxiliary gas flow rates are adjusted to approximately 20 and 1.5 L/min of air, respectively. After the air-ICP is operating, the Roots blower speed is increased to approximately 1100 rpm, the gas inlet line is removed (and the inlet is capped), and the sampling pump is turned on. A valve on the inlet to the sampling pump and the speed of the Roots blower are adjusted so that proper gas sample flow rates through the Teflon sampling system and into the axial channel of the ICP torch are established. Gas flow rates of approximately 30 standard L/min and 1 standard L/min, through the sampling chamber and into the axial channel of the ICP, respectively, were used during laboratory testing.

For laboratory testing of the continuous sampling air-ICP system, the sampling chamber was open on one end, so room air was drawn through the chamber and into the air-ICP. Aqueous solution standards of metals were introduced into a CETAC Technologies U5000-AT ultrasonic nebulizer, and the dry aerosol output from the nebulizer was connected to the port on the inlet side of the sampling chamber (nebulizer spike in Figure 3). This arrangement was used for introducing metal aerosols into the sampling chamber and the air-ICP system for calibration and monitoring experiments. For the laboratory testing described below, the sampling chamber was operated at room temperature, and the sampling probe and the 12' long heat-traced Teflon line were not connected to the sampling system.

2.4. Reduced-Pressure Continuous Sampling Air-ICP System at DIAL

During the week of 12 September 1999, the continuous sampling air-ICP system was tested at DIAL. This was the first field test of this system. These tests were performed on the combustion test stand at DIAL, a fuel oil-air furnace with capabilities for air preheating, introduction of fly ash mixed with the fuel, and introduction of heavy metal aerosols in the exhaust line. Figure 4(a) shows the air-ICP system in front of the scaffolding, connected to the combustion test stand. During the test at DIAL, the furnace on the combustion test stand was operated with 227 kg/h of air and 4.5 kg/h of fuel oil, which produced a gas flow in DIAL's 8"-diameter, schedule-80 pipe (19.4-cm inside diameter) of approximately 3000 standard L/min. At the sampling point, the gas temperature was 235°C, with a velocity of approximately 3.1 m/s. The air-ICP CEM sampling probe was installed in a vertical section of the exhaust line, several meters downstream from the water-cooled exhaust line, as shown in Figure 4(b). In order to minimize differences between sample concentrations at various locations in the exhaust line due to drop out of particles and particle segregation, RM-29 sampling occurred at a port in the vertical pipe across from and within a few centimeters of the sampling port for the air-ICP. At the sampling point, the exhaust gas was flowing vertically

down the pipe. About two meters above the sampling point, a pneumatic air-driven nebulizer was installed at the top of the vertical section to introduce appropriate concentrations of aqueous solutions of Be, Cd, Cr, Pb, and Hg into the exhaust gases. During the time that the CEM was collecting data and toxic metals were being introduced into the exhaust stream, samples of the exhaust stream were collected using RM-29. The collected samples have been sent to a certified laboratory for quantitative analysis.

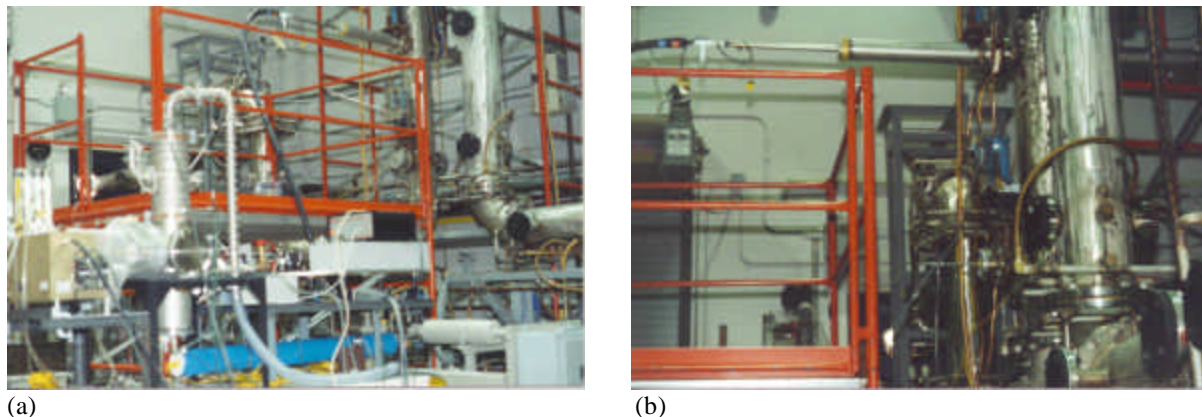


Figure 4. (a) The continuous sampling air-ICP system connected to the combustion test stand at DIAL. Near the top of the photograph, the glass-lined sampling probe is shown inserted into a vertical section of the test stand and connected to the black heat-traced sample line. (b) The air-ICP sampling probe, inserted into the stack, showing the nebulizer spike location– the white Teflon tee between the probe and the sample line.

The details of the sampling system for the air-ICP are described in Section 2.2. The temperature of the gases sampled from the exhaust line at DIAL was 235°C, which is within the temperature range specification of the EPA isokinetic sampling probe that was used, but is too high for the Teflon sample line. This line transports the gas stream to the Teflon sampling chamber, from which a secondary sample is drawn for introduction into the ICP torch, inside the reduced-pressure enclosure. Although the sampling probe has an integral heater, it was not used. Instead, the sampled gas was allowed to cool to a temperature of 125°C in the probe before entering the Teflon sample line. From that point, the sample line was electrically heated to maintain a temperature in the range of 105 to 120°C, to prevent the condensation of water in the sampled gas. For this test, because of the large air-to-fuel ratio employed at DIAL, the water content of the exhaust gas was only about 5%. This corresponds to a dew-point temperature of about 35°C, so the Teflon sampling system could presumably have been operated at a lower temperature with no condensation in the sample gas stream. A sampling rate from the exhaust pipe of 22 standard L/min was employed. The gas pressure in the test stand at the sampling point was about 1.5 kPa (15 cm of water) below atmospheric pressure. To extract the 22 L/min of sample flow from the stack, the plasma enclosure had to be operated at a lower pressure than was used during laboratory testing of the air-ICP system. The Roots blower was operated at a higher speed (about 2400 rpm) and at a pressure of 4.4 kPa (45 cm of water) below ambient atmospheric pressure during the testing at DIAL.

When the air-ICP system was connected to the stack during testing at DIAL, significant fluctuations in the sample gas flow into the plasma occurred. The reason for the sample flow variation was the random pressure variation in the exhaust pipe, at least 10% variation, on a one-second time scale. The magnitude of the stack pressure variation at DIAL was unexpected, and the sampling system was not able to adequately compensate for the fluctuations in flow that occurred. When the air-ICP system was connected to the stack, a sample flow to the axial channel of the torch corresponding to a differential pressure of approximately 0.3" of water was used. However, due to stack flow and pressure variations, the differential pressure indicated by the oil-filled manometer varied between approximately 0.25" to 0.35" of water, with excursions as low as 0.2" and as high as 0.4". This large variation in gas flow rate into the axial channel of the air-ICP (from approximately 1.0 to 1.4 L/min) caused obvious fluctuations in the intensity of the plasma during operation of the air-ICP and during collection of analytical data at DIAL.

3. Results and Discussion

3.1. Laboratory Testing of the Continuous Sampling Air-ICP System

A limited amount of analytical laboratory data was acquired using the continuous sampling air-ICP system prior to the DIAL test, due to the recent assembly of the Teflon sampling chamber and incorporation of the chamber with the reduced-pressure air-ICP system. The testing that was done focused on the detection of the metals As, Be, Cd, Cr, Hg, and Pb, introduced into the sampling chamber and air-ICP by nebulizing single-element solutions of the metals using an ultrasonic nebulizer. Optical emission signals from the metals introduced into the air-ICP were detected using the Ames AOTF-echelle spectrometer system, including acquiring spectral data, performing calibration experiments, and conducting time-scan and continuous monitoring tests.

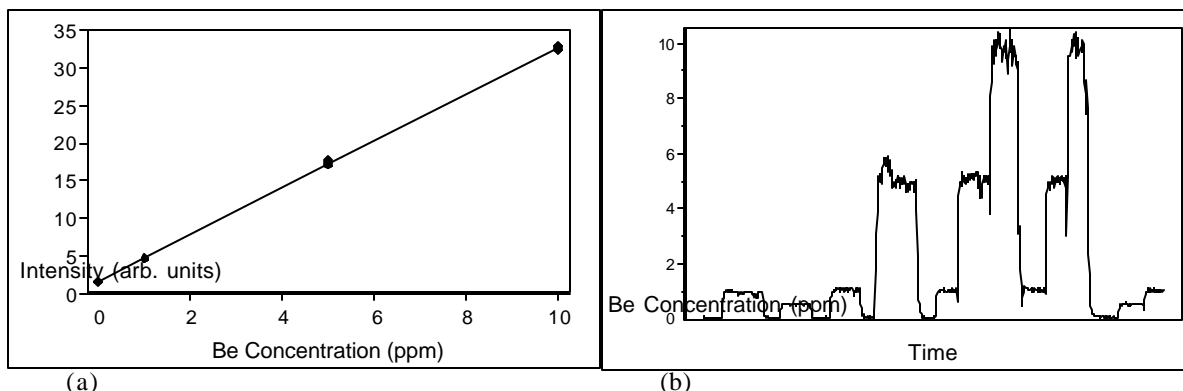


Figure 5. (a) Calibration curve obtained for the Be (II) 313.04-nm emission line, obtained by nebulizing solutions containing 0, 1, 5, and 10 ppm beryllium. (b) Continuous monitoring of the Be (II) 313.04-nm line, for solutions containing 0, 0.5, 1, 5, and 10 ppm beryllium.

An example of the calibration and continuous monitoring experiments performed is shown in Figure 5, for beryllium. Figure 5(a) is a calibration curve generated for the Be (II) 313.04-nm emission line. This calibration curve was obtained by introducing solution standards containing 0, 1, 5, and 10 ppm Be into the ultrasonic nebulizer, with the aerosol from the nebulizer introduced into the port (nebulizer spike) on the inlet side of the sampling chamber. Figure 5(b) is a plot showing continuous monitoring of the Be (II) 313.04-nm emission line, performed after calibration. This data was obtained by nebulizing solutions containing 0, 0.5, 1, 5, and 10 ppm Be, over a period of time in excess of 30 minutes (1000 data points at a signal integration time of 2-s per point). The values in Figure 5 are the solution concentrations, introduced into the ultrasonic nebulizer, not the aerosol concentrations introduced into the air-ICP. Based on the solution flow rate to the nebulizer (1 mL/min), the approximate nebulizer efficiency (12.5% assumed, based on a previous measurement), and the gas flow rates through the nebulizer (1 L/min) and the sampling chamber (30 L/min), the approximate aerosol concentrations for 1, 5, and 10 ppm solution concentrations are 4, 20, and 40 $\mu\text{g/dscm}$, respectively.

The signal stability for the beryllium monitoring data shown in Figure 5 is approximately 2-5% relative standard deviation (rsd), for the time periods that beryllium was introduced into the sampling chamber and air-ICP (the signal plateaus in Figure 5(b)). Some of the source of this signal variation may be attributed to minor fluctuations in the primary and secondary sample flow rates due to pressure fluctuations caused by the sampling pump and Roots blower. However, additional sources of drift and signal variation may be attributed to variations in the air supply gas pressure (the laboratory building air supply was used directly, with no additional pressure regulation) and to variations in the RF power output of the ICP generator (a decades-old ICP system). The initial signal spike in the first 5-ppm Be monitor data shown in Figure 5(b) is believed to be due to an increase in the RF power output of the ICP generator. A detection limit of 0.04 ppm Be (approximately 0.16 $\mu\text{g/dscm}$) is calculated from the beryllium monitor data, by dividing three times the standard deviation of the blank (0 ppm Be introduced in Figure 5(b)) by the slope of the calibration curve. Detection limits for a number of other metals introduced into the reduced-pressure air-ICP using this sampling system were obtained during the course of the initial laboratory testing, by performing time-scan monitoring of ICP emission signals. Detection limits of approximately 12, 4, 200, and 80 $\mu\text{g/dscm}$ for chromium (Cr (II) 283.56 nm), manganese (Mn (II) 260.57 nm), mercury (Hg (I) 253.65 nm)

and lead (Pb (I) 405.78 nm), respectively, were obtained using 1-s detector integration times. These detection limits are about the same as those obtained previously for the air-ICP and AOTF-echelle spectrometer system.¹ Detection limits for arsenic and cadmium are poorer than those reported previously, due to the low output power of the AOTF RF synthesizer-amplifier system used during laboratory testing at wavelengths less than 235 nm, the region of the strongest emission lines for As and Cd.

3.2. Air-ICP CEM Testing at DIAL

Prior to collecting data at DIAL, the reduced-pressure air-ICP system needed to be assembled and integrated into the combustion test stand. This was done primarily during the first two days at DIAL. This initial setup included coupling the reduced-pressure plasma enclosure to DIAL's generator and AMN, a compact, solid-state, 27 MHz, 3-kW ICP system from Seren Industrial Power Systems. Since this RF generator had not been used with the reduced-pressure air-ICP system previously, some time was required to accomplish this task. A number of different load coils for the ICP torch were made and tested for operation of the reduced-pressure plasma with the Seren system. The ICP could not successfully be switched from argon- to air-operation using a three-turn load coil similar to the one used at AL with the Plasma-Therm ICP system. A four-turn load coil was tried, but the switchover from argon to air could not reliably be achieved using this coil. A five-turn coil was required for operation of the reduced-pressure air-ICP with the Seren generator and AMN and was used during the testing at DIAL.

The AOTF-echelle spectrometer that had been delivered to DIAL in FY98 was initially incorporated with the reduced-pressure plasma system for detecting optical emission from metals in the sampled gas stream, introduced into the air-ICP CEM. After some time spent aligning and trying to optimize signal intensities observed using the AOTF-echelle spectrometer, it became apparent that the AOTF was not functioning as well as it had been when the system was initially delivered to and tested at DIAL during FY98. Very low signal intensities were observed for AOTF-selected emission lines, which meant that either the efficiency of the AOTF crystal was much lower than that observed previously or that the RF power supplied by the AOTF controller was too low. (Preliminary inspection of this AOTF at AL after the testing at DIAL indicates that the RF driver is operating normally, so the AOTF crystal is apparently no longer functioning as well as it initially did.) As a result, the AOTF was removed and replaced by a 0.2-m focal-length monochromator (ISA model H20), which was used as a pre-filter for the echelle spectrometer for the data collected during the testing at DIAL. Relatively little optimization of the alignment of the echelle spectrometer, using the 0.2-m monochromator as a pre-filter was done, due to the time constraints of the testing at DIAL. The limit of detection (LOD) determined for Be, Cd, and Hg during the testing at DIAL are worse than laboratory values obtained previously using the air-ICP. The LODs listed below are not the best that can be achieved for an air-ICP CEM system, but are simply the values determined for initial field testing of a system during which time some compromise conditions were used because of time limitations.

The continuous sampling air-ICP system was in operation throughout the day (approximately 7 hours continuous operation) on September 16. During the day, continuous emission monitoring of metals in the DIAL exhaust stack using the air-ICP CEM system was performed before, during, and after the collection of two RM-29 samples by DIAL personnel, with one sample set collected in the morning and one in the afternoon. Prior to the first RM-29 sample collection, and before the operating air-ICP system was connected to the stack (before connecting the heat-traced Teflon sample line to the sampling probe), testing of the air-ICP system for the detection of Be, Cd, Cr, Hg, and Pb was performed. This was done by nebulizing solution standards using an ultrasonic nebulizer, introducing the dry aerosol output from the nebulizer into the port on the sample line (Teflon tee in Figure 4(b)). This spiked gas stream was sampled using the Teflon sampling system, and introduced into the axial channel of the air-ICP. Optical emission from the metals introduced into the reduced-pressure air-ICP was detected using the echelle spectrometer system. Solution standards of 100 ppm Be, Cd, Cr, and Pb and 1000 ppm Hg were introduced and detected. Spectral data files were acquired and time-scan emission monitoring was performed. An example of the time-scan monitoring is shown in Figure 6 for Be. The Be (II) 313.04-nm emission signal was detected using a 1-s per point integration time, for the introduction of 100 ppm Be and for a water blank solution. From the signal-to-noise ratio of the time-scan data in Figure 6, a solution concentration limit of detection (LOD) of 0.59 ppm Be is obtained (3- σ standard deviation of the blank definition). Based on the solution flow rate to the ultrasonic nebulizer (1.9 mL/min), the approximate nebulizer efficiency (15%), and the gas flow rates through the nebulizer (1 L/min) and the sampling chamber (22 L/min), the approximate corresponding aerosol LOD is 7.7 μ g/dscm for Be. In a similar fashion, detection limits for cadmium (Cd (I) 228.80 nm), chromium (Cr (I) 359.35 nm), mercury (Hg (I)

253.65 nm), and lead (Pb (I) 405.78 nm) were determined for the air-ICP system, without the heat-traced sample line connected to the DIAL stack. The solution LODs for Cd, Cr, Hg, and Pb were 11.6, 0.092, 52.3, and 0.96 ppm, respectively, which correspond to aerosol concentrations of 150, 1.2, 680, and 12.5 $\mu\text{g/dscm}$ for these four elements. The magnitude of the signal intensity for the 100-ppm Cr solution saturated the CCD detector, for the 1-s integration time used. This fact was not realized during acquisition of the time-scan data. As a result, the LOD for Cr is actually lower than the 1.2- $\mu\text{g/dscm}$ value listed above. The LODs for Be, Cd, and Hg obtained during the testing at DIAL are worse than the values obtained previously in laboratory tests of an air-ICP system using a similar echelle spectrometer. The poorer LOD for Be during the testing at DIAL is thought to be primarily a plasma observation height issue. The degraded performance for Cd and Hg may be a UV-chromatic aberration effect resulting from less-than-optimum alignment of the 0.2-m monochromator – echelle spectrometer system during the DIAL test.

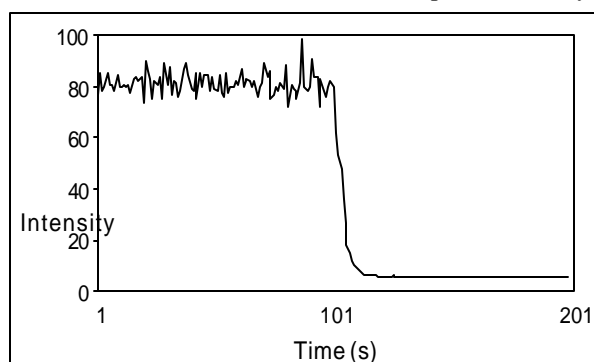


Figure 6. Time-scan emission monitoring for beryllium (Be (II) 313.04 nm), obtained for the introduction of a 100-ppm Be solution and a water blank, using the ultrasonic nebulizer (stack not connected).

Following these initial experiments, the heat-traced Teflon sample line was connected to the stack (connected to the sampling probe that extended into the stack), so that on-line monitoring of metals introduced into the stack could be performed using the air-ICP CEM. After the sample line was connected to the stack, acquisition of the first RM-29 sample of the day began. During this time, spectral data acquisition and time-scan emission monitoring was performed using the air-ICP and echelle spectrometer system. Time-scan monitoring data was collected for Be, Cr, and Pb during the RM-29 run. Cadmium and Hg were not detected in the sampled stack gas. Based on the relatively poor detection limits for Cd and Hg above, it is not surprising that these two metals were not detected in the stack gas stream, assuming that the levels of the five metals introduced into the stack were approximately equal. Due to the significant variations in the sampled gas flow rate into the axial channel of the ICP when the air-ICP sampling system was connected to the stack (see discussion in Section 2.4), only time-scan emission monitoring was performed during the RM-29 sampling. Calibration experiments (comparable to that shown in Figure 5(a)) were not conducted because of the significant variation in signal intensities measured for Be, Cr, and Pb when the stack was connected. (In retrospect, however, based on the data presented below, these calibration experiments could have been done if sufficient time-averaging of the signal intensities had been used. The continuous sampling capability of this air-ICP system allows the use of extended time periods for data acquisition, when necessary, and more easily than systems that introduce the sampled gas stream intermittently, using a sampling loop and injection valves.) After the first RM-29 sample acquisition was completed, a series of time-scan monitoring and calibration spiking experiments were performed for Be, Cr, and Pb. The calibration spiking data for Cr is shown in Figure 7(a). The initial time-scan intensity in Figure 7(a), approximately the first 75 s (or 75 points, since the integration time was 1-s per point), is the signal detected for Cr while metals were being introduced into the stack. After this, the metals solution was replaced with water, so that a water blank was introduced into the stack (points 75-400). From points 400-1000, a series of solutions containing increasing concentrations of Cr (5, 10, 50, and 100 ppm) were nebulized using the ultrasonic nebulizer and introduced into the sampled gas stream at the nebulizer spike location, in order to perform on-line calibration. The increase in the signal variation resulting from the sample-flow variations that occurred during the testing at DIAL when the air-ICP was connected to the stack is very obvious in Figure 7(a). The signal variation for the signal plateaus in the time-scan stack monitoring data was typically in the range of 20-60% rsd for Cr, Pb, and Be, for 1-s detector integration times. For Cr, the rsd was typically about 20% (Figure 7(a) and other time-scan monitoring data not shown). For time-scan data acquired when the air-ICP was not connected to the stack (such as that for Be in Figure 6 above), the rsd was in

the 3-5% range. The calibration curve in Figure 7(b) was generated from the time-scan data for Cr, using signal intensities that were averaged over as many time-scan data points as possible. The Cr signals measured for the 50- and 100-ppm spikes in Figure 7(a) were suppressed, due to saturation of the CCD detector for the 1-s integration time used. Therefore, for the Cr calibration curve shown in Figure 7(b), these points were not included in the linear regression fit of intensity vs. concentration. The measured Cr intensity corresponds to a solution concentration of 5.7 ppm Cr for the stack metals signal in Figure 7(a), points 1-75, using the Cr calibration curve. Based on the solution flow rate to the ultrasonic nebulizer (1.4 mL/min), the approximate nebulizer efficiency (15%), the gas flow rates through the nebulizer (1 L/min) and the sampling chamber (22 L/min), and 5% water content in the stack gas, the corresponding Cr aerosol concentration is approximately 57 $\mu\text{g/dscm}$. For the Cr signal intensity in Figure 7(a) measured when metals were introduced into the stack (points 1-75) and the 3- σ standard deviation for the water blank (points 300-400 approximately), the signal is a factor of approximately 13 times higher than the detection limit. This corresponds to a Cr aerosol LOD of approximately 4.4 $\mu\text{g/dscm}$. The Cr signal intensities measured during the RM-29 sampling were actually slightly higher than that measured for the first 75 points in Figure 7(a). The average signal intensity measured for these prior time-scan data files, acquired during the RM-29 sampling, corresponds to a Cr solution concentration of 6.3 ppm, or 63 $\mu\text{g/dscm}$ Cr during the RM-29 run. This concentration is calculated assuming that the experimental conditions were constant and stable throughout the course of the acquisition of all of the Cr time-scan data. Based on the standard deviation of the signal levels detected during the RM-29 sampling and later, for the Cr calibration spiking data, the determined concentrations may not be statistically different.

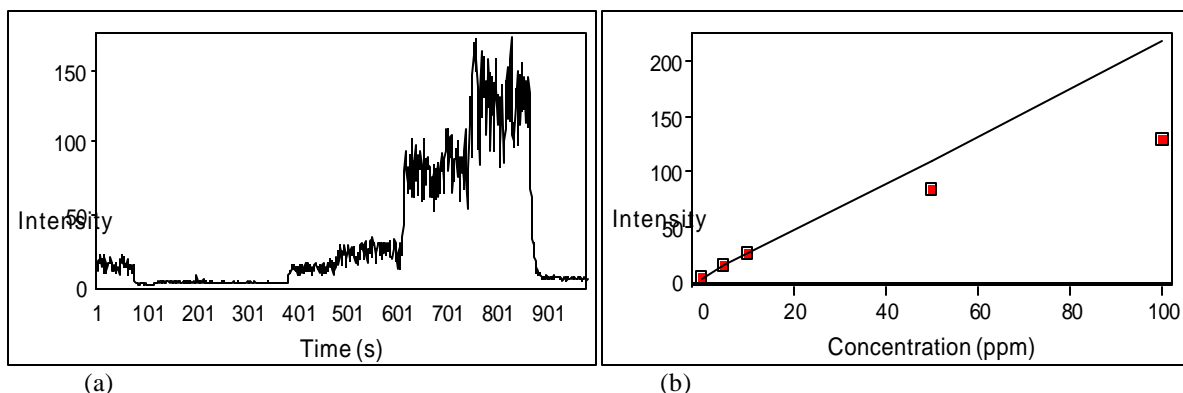


Figure 7. (a) Time-scan monitoring data for chromium (Cr I) 359.35 nm), with metals introduced into the stack, water introduced into the stack, and Cr calibration spikes added to the sampled gas stream. (b) Calibration curve for Cr, generated from the time-scan data.

For Be and Pb, similar calibration spiking experiments were performed, with metals introduced initially into the stack, followed by water, and then metal aerosol spikes resulting from the introduction of 5, 10, 50, and 100 ppm solutions, nebulized using the ultrasonic nebulizer. The time-scan data and corresponding calibration curves for Be and Pb are shown in Figure 8. For beryllium (Be II) 313.11 nm), the signal intensity variations are severe, using a 1-s integration time, approximately 60% *rsd*. However, by averaging the signal intensities over approximately 100 points for each region in Figure 8(a), a reasonable calibration curve (Figure 8(b)) can be generated, despite the large variations in time-scan data. A larger signal variation for the Be time-scan data was observed during the testing at DIAL and is evident in Figure 8(a), compared that observed for Cr in Figure 7(a). The larger *rsd* for Be signals compared to those for Cr and Pb is presumably due to the fact that the Be line is an ion line, while the Cr and Pb lines are atom lines, and that the sample flow variations into the air-ICP affected ion lines more significantly than atom lines, at least for the plasma observation height used during the testing at DIAL. Using the Be calibration curve, the measured Be intensity is equivalent to a solution concentration of 5.2 ppm Be, for the stack metals signal in Figure 8(a), points 1-190. The corresponding aerosol concentration is approximately 52 $\mu\text{g/dscm}$ Be. This concentration is close to the detection limit for Be, for the experimental conditions during the testing at DIAL. The signal-to-noise ratio for the Be time-scan data (points 1-190 for the Be signal and points 200-300 for the standard deviation of the water blank in Figure 8(a)) is less than 2. As discussed above for Cr, the Be signal intensities measured during the RM-29 run were actually slightly higher than that measured during the spiking experiment (points 1-190 in Figure 8(a)). The average signal intensity measured for these prior time-scan data files,

acquired during the RM-29 sampling, corresponds to a Be solution concentration of 7.3 ppm, or approximately 73 $\mu\text{g/dscm}$ Be.

For the calibration spiking experiments for lead (Pb (I) 405.78 nm), an integration time of 3-s per point was used, which lowers the signal variation of the time-scan data in Figure 8(c) to about 20% *rsd*. For the calibration curve in Figure 8(d), the 100-ppm Pb spike solution data was not included in the linear regression fit of the time-scan data. The error in the fit of the calibration curve was improved significantly by excluding this point. The reason for the lower signal intensity (19% lower than the fitted intensity) for the 100-ppm Pb spike solution is unknown. It is not a detector saturation problem, such as that for Cr in Figure 7, but apparently due to instability from an unknown source. A solution concentration equivalent to 4.4 ppm Pb is calculated for the stack metals signal in Figure 8(c), points 1-50, using the Pb calibration curve. The corresponding Pb aerosol concentration is approximately 44 $\mu\text{g/dscm}$. The signal-to-noise ratio of the Pb time-scan data in Figure 8(c) is a factor of approximately 3, calculated for the Pb signal intensity (points 1-50) and the 3- σ standard deviation of the water blank (points 60-100 in Figure 8(c)). Therefore, the detection limit for Pb is approximately 15 $\mu\text{g/dscm}$ for the conditions used during the testing at DIAL. During the RM-29 sampling period, higher signal intensities (than that shown in Figure 8(c), points 1-50) were measured for Pb in the sampled stack gas. The average intensity for these prior time-scan data files corresponds to a solution concentration of 5.6 ppm Pb, or approximately 56 $\mu\text{g/dscm}$ for Pb, during the RM-29 sampling. For Pb, different CCD detector integration times were used for the calibration spiking experiment (Figure 8(c)) and the prior time-scan data files acquired during the RM-29 run. The 56- $\mu\text{g/dscm}$ value for Pb was calculated assuming that the signal intensities for Pb and for the blank scale linearly with detector integration time.

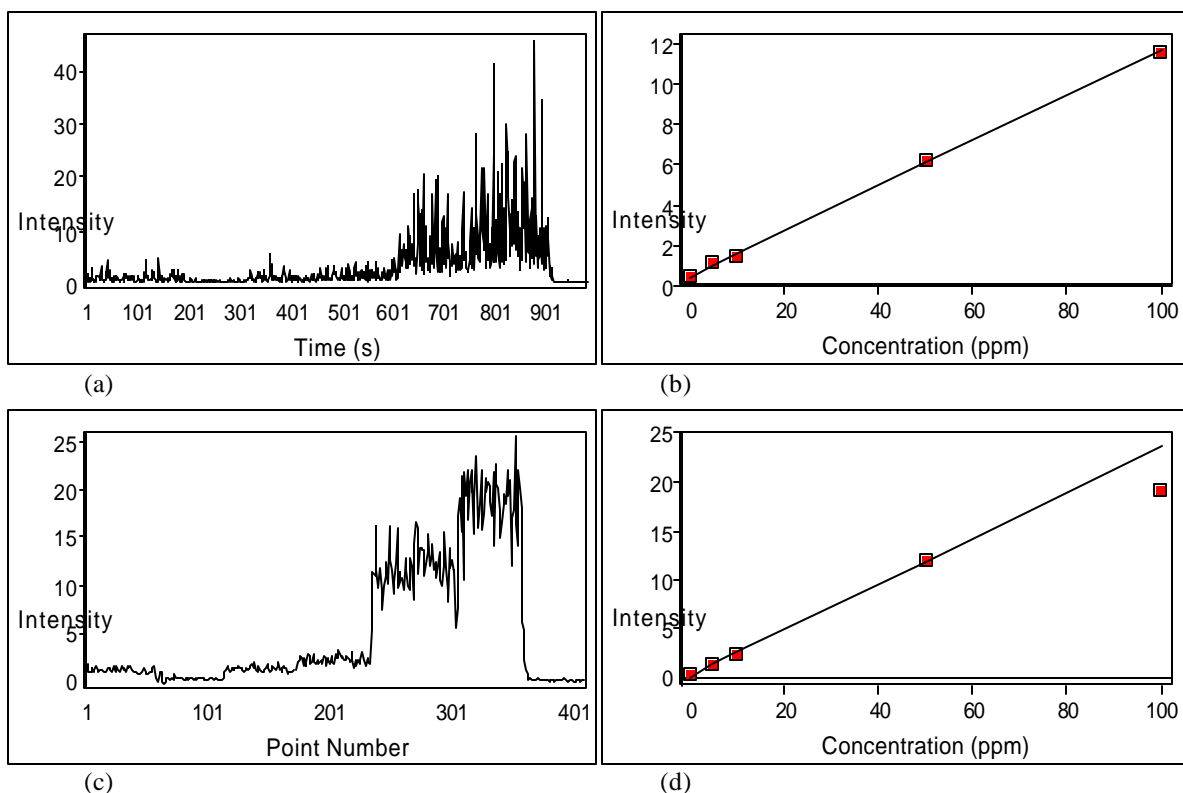


Figure 8. Time-scan calibration spiking data for (a) beryllium (Be (II) 313.11 nm) and (c) lead (Pb (I) 405.78 nm), with metals introduced into the stack, water introduced into the stack, and calibration spikes added to the sampled gas stream. Calibration curves for (b) Be and (d) Pb, generated from the time-scan data.

During acquisition of the second RM-29 sample set on September 16, metals were introduced into the stack at levels that were presumably identical to those used during the first run. The air-ICP signal intensities for Be, Cr, and Pb during the RM-29 sampling were approximately equal to those measured earlier in the day. Time-scan

monitoring for Cr and Be during the second RM-29 run is shown in Figure 9. These time-scan data files were acquired using a detector integration time of 3-s per point, so the rsd of the signal variation is less than that shown above for Cr in Figure 7(a) and Be in Figure 8(a). For Cr in Figure 9(a), the rsd is 12.3%. In Figure 9(b), the rsd for the Be signal is 35% and 47% for points 1-39 and points 60-178, respectively. For the approximate 1-minute time period between points 39 and 60, the Be signal dropped significantly. This decrease resulted from a large increase in the sample gas flow into the air-ICP system, while momentary adjustments in the operating conditions of the stack were made. These normal variations in stack operations were made throughout the testing period, with resulting obvious changes noted in the time-scan data collected using the air-ICP and in the differential pressure indicated by the oil-filled manometer on the inlet to the axial channel of the plasma. Fortunately, after these momentary changes in stack operating conditions occurred, the signal levels detected using the air-ICP system returned to values observed prior to the stack fluctuation. A second example of this is shown in time-scan data in Figure 7, during the initial time that the water blank was introduced into the stack, approximately points 80-125 in Figure 7(a). After the RM-29 sampling was complete, calibration spiking experiments similar to those shown in Figures 7 and 8 were unfortunately not done for Be, Cr, and Pb. Instead, time-scan monitoring for Cd and Hg, for on-line spiking experiments (with the stack connected) were performed. However, since Cd and Hg were not detected in the sampled stack gas during the RM-29 run, the results for these spiking experiments are of less value than the data for Be, Cr, and Pb would have been, had this data been collected. Actually, this calibration spiking should have been done throughout the entire day, before, during, and after the RM-29 sampling. If these experiments had been done during the entire testing period, more useful and meaningful data would have been collected. These results would have provided some information on whether slightly different signal intensities measured during the RM-29 sampling were due to variations in the operating conditions for the air-ICP plasma and sampling system, or whether the signal differences were due to variations in the concentrations of the metals introduced into the stack. Approximate metal concentrations in the stack throughout the RM-29 run could have been calculated from these calibration spiking experiments, but some assumptions regarding the signal levels for the blank would have to have been made.

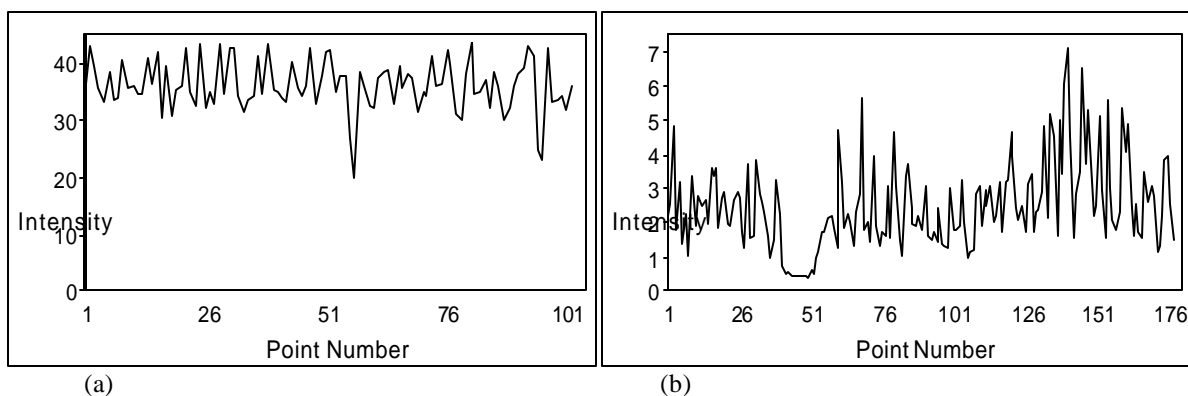


Figure 9. Time-scan monitoring for (a) chromium (Cr (I) 359.35 nm) and (b) beryllium (Be (II) 313.11 nm) during the second RM-29 sampling conducted on September 16. The detector integration time used was 3-s per point.

4. Future Work

One of the most significant issues that was experienced during the field testing at DIAL was the substantial amount of sample flow variation to the plasma, as a result of the pressure fluctuations in the exhaust line of the combustion test stand. During future testing at DIAL, this situation will be compensated for by installing a sample-flow ballast between the Teflon sampling chamber and the sampling pump. The ballast, a large empty volume, will provide a nearly constant pressure reservoir for secondary sampling into the plasma, thereby providing a nearly constant sample flow to the air-ICP. The ballast will be installed between the pump and the secondary sampling region in the Teflon chamber, so that the isokinetic sampling in the chamber will not be affected by pressure fluctuations. A short, large diameter tube (on the order of 2-cm diameter and 10-cm long) will be used to connect the sampling chamber to the ballast. This should provide a high flow conductance of gas to couple closely the nearly constant pressure in the ballast with the sampling chamber pressure. A ballast volume of about 33 L would result in a flow time constant of 99 s, for a sampling rate of 20 L/min. This time constant corresponds to a maximum pressure variation of about 1% per second. The Teflon sampling chamber has a volume of about 1/3 of a

liter, corresponding to a time constant of about 1 s, which is too short to significantly reduce the pressure variations of the exhaust pipe at DIAL. Another possible improvement involves increasing the velocity of the sample gas in the heated transfer line and decreasing the conductance of this line. Reducing the diameter of the transfer line will increase the velocity and reduce the conductance of the flow of sampled gas from the exhaust pipe to the sampling chamber. This change will decrease the magnitude of the pressure variations in the sampling chamber. It should also have the effect of decreasing the transit time of the sampled gas from the exhaust pipe to the ICP torch, presumably resulting in greater sample integrity and reduced particle fall out.

Additional work will be done to characterize the capabilities of the system and to improve its sensitivity. Also, the current pumping system consisting of the Roots blower needs to be downsized. The current pump assembly has too much capacity and is almost as large as the rest of the reduced-pressure air-ICP sampling and spectrometer system.

5. Conclusions

A continuous sampling air-ICP system has been designed for monitoring metals as a continuous emission monitor (CEM). The system consists of an air plasma that is operated inside a metal enclosure at a pressure slightly less than atmospheric pressure, using a Roots blower to draw sample continuously into the air-ICP. A Teflon sampling chamber has been designed to allow continuous sampling of metal aerosols from an exhaust stack or process line for introduction into the plasma, from which optical emission from the metals in the sampled gas stream can be continuously monitored using a spectrometer system such as the AOTF-echelle spectrometer. The initial laboratory testing of this air-ICP system has shown the functional requirements necessary for CEM operation. The first field test of the instrument was performed at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University in September 1999. Concentrations of Be, Cd, Cr, Hg, and Pb were added to the stream of exhaust gases from the fuel oil-air furnace on the combustion test stand, and Be, Cr, and Pb were measured with the continuous sampling air-ICP CEM at the ~ 50 $\mu\text{g/dscm}$ level during the test. Additional laboratory and stack monitoring tests will be performed in the near future to more fully characterize the capabilities of the system for CEM applications and to correct the weaknesses found during the first field test.

Any assessment of the field test should examine each of the four tasks as stated in the introduction to this report. All of these tasks were accomplished, although with varying degrees of success, and with results that ultimately impacted the overall performance of the system during this test. First, we planned to integrate the reduced-pressure plasma system with the matching network and solid-state RF power supply at DIAL. This task was successfully accomplished. What we learned is that, as expected, the additional length of the load-coil leads and the steel enclosure change the impedance of the load for the RF supply. It is necessary to modify the ICP load coil to adapt to different supplies. We were prepared for this need and accomplished our goal. Second, we planned to integrate the AOTF-echelle spectrometer, which was delivered to DIAL in FY98, with the reduced-pressure air-ICP system. This was accomplished. However, due to the failure of a component of the AOTF, we were forced to modify the spectrometer for the duration of the test, by using a small grating spectrometer instead of the AOTF as a pre-disperser for the echelle spectrometer. We had anticipated this possibility and brought the small spectrometer along as a backup. This substitution allowed the test to go forward, although time limitations and problems associated with aligning the modified spectrometer ultimately led to poorer detection limits for Be, Cd, and Hg during the test at DIAL, compared to previous laboratory values obtained using the air-ICP system. The detection limits determined during the test should not be considered indicative of the capabilities of either the AOTF-echelle technology or the reduced-pressure air-ICP. Third, we planned to assemble the CEM system and attach it to the test stand facility at DIAL. This goal was successfully accomplished. The system was assembled in the high bay area of the DIAL facility, and the probe was mated to the exhaust line of the fuel oil-air burner. Fourth and finally, we planned to use the CEM to monitor metals in the burner exhaust line. This goal was accomplished. The CEM was used to monitor for three of the five target metals while DIAL staff simultaneously collected RM-29 samples for later analysis. These analyses are not yet complete, but when they are, we will amend this report with those results and comparisons with our data. The performance of the CEM in this stage was limited by the problems with the modified spectrometer and by an unanticipated problem with pressure fluctuations in the exhaust stream. The spectrometer and alignment issues were unavoidable at the time and will be corrected in future field tests. The pressure fluctuation issue will be corrected with some fairly minor modifications to the sampling system. Overall, the test was extremely successful in that we accomplished all of the ambitious goals that we set out for ourselves, and we learned some valuable lessons that will be used to improve the system in future tests and demonstrations.

6. Acknowledgments

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University, under contract number W-7405-Eng-82. This work was supported by the U.S. Department of Energy, Office of Environmental Management, Office of Science and Technology, through the Characterization, Monitoring, and Sensor Technology Crosscutting Program.

7. References

1. D. P. Baldwin, D. S. Zamzow, D. E. Eckels, and G. P. Miller, "AOTF-Echelle Spectrometer for Air-ICP-AES Continuous Emission Monitoring of Heavy Metals and Actinides," in *Environmental Monitoring and Remediation Technologies*, T. Vo-Dinh and R. L. Spellicy (Eds.), Proceedings of SPIE Vol. 3534, pp. 478-486, 1999.
2. D. P. Baldwin, D. S. Zamzow, D. E. Eckels, and G. P. Miller, "A Continuous Sampling Air-ICP for Metals Emission Monitoring," submitted for publication in the proceedings of the International Conference on Environmental Monitoring and Remediation Technologies II, Proceedings of SPIE Vol. 3853, September, 1999.
3. Code of Federal Regulations, Part 60, Appendix A (61 FR 18262 4/25/96).
4. A. Montaser, "Assessment of the Potentials and Limitations of Plasma Sources Compared to ICP Discharges for Analytical Spectrometry", in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser and D. W. Golightly (Eds.), 2nd edn., VCH Publishers, New York, 1992, Chapter 1.
5. R. K. Winge, V. J. Peterson, and V. A. Fassel, "Inductively Coupled Plasma – Atomic Emission Spectroscopy: Prominent Lines," *Appl. Spectrosc.* **33**, pp. 206-219, 1979.
6. G. A. Meyer and P. N. Keliher, "An Overview of Analysis by Inductively Coupled Plasma -Atomic Emission Spectrometry", in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser and D. W. Golightly (Eds.), 2nd edn., VCH Publishers, New York, 1992, Chapter 10.
7. G. A. Meyer and M. D. Thompson, "Determination of Trace Element Detection Limits in Air and Oxygen Inductively Coupled Plasmas," *Spectrochim. Acta* **40B**, pp. 195-207, 1985.
8. A. Montaser, K. D. Ohls, and D. W. Golightly, "Inductively Coupled Plasmas in Gases Other Than Argon", in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser and D. W. Golightly (Eds.), 2nd edn., VCH Publishers, New York, 1992, Chapter 19.
9. D. P. Baldwin, D. S. Zamzow, and A. P. D'Silva, "Detection Limits for Hazardous and Radioactive Elements in Airborne Aerosols Using Inductively Coupled Air Plasma - Atomic Emission Spectrometry," *J. Air & Waste Manage. Assoc.* **45**, pp. 789-791, 1995.
10. G. P. Miller, Z. Zhu, D. P. Baldwin, and D. S. Zamzow, "Final Report. DOE/EPA. Test Results from the DOE/EPA sponsored Multi-metals Continuous Emission Monitor Demonstration. A Portable ICP-AES System for On-Line Monitoring of Toxic Metals," 25 pages, 1997.
11. M. D. Seltzer and G. A. Meyer, "Inductively Coupled Argon Plasma Continuous Emissions Monitor for Hazardous Air Pollutant Metals," *Environ. Sci. Technol.* **31**, pp. 2665-2672, 1997.
12. A.-M. Gomes, J.-P. Sarrette, L. Madon, and A. Almi, "Continuous Emission Monitoring of Metal Aerosol Concentrations in Atmospheric Air," *Spectrochim. Acta* **51B**, pp. 1695-1705, 1996.

Appendix

Analytical results for the RM-29 samples collected during the testing at DIAL were received after completion of this air-ICP CEM report. These results were obtained by a certified, off-site analytical laboratory, using standard analysis methods to determine the metal concentrations for the solutions collected during the DIAL test. The results for Be, Cd, Cr, Pb, and Hg are listed in Table 1, for the two RM-29 sample sets collected on September 16, 1999. The values for all five metals are fairly consistent, with most of the determined values between 60 and 75 $\mu\text{g/dscm}$. Since identical concentrations of all five metals were introduced into the stack during the testing at DIAL for both RM-29 runs, the similarity of the determined values is expected. For run 1, the average value for the five metals is 68.2 $\mu\text{g/dscm}$, and the relative standard deviation (rsd) is 8.2%. For run 2, the average value for the four metals (Hg was not determined) is 74.3 $\mu\text{g/dscm}$, and the rsd is 13.3%. The higher average and rsd for run 2 are primarily due to the higher value for Cd, 87 $\mu\text{g/dscm}$ compared to 75 $\mu\text{g/dscm}$ for run 1.

The aerosol concentrations determined by continuous sampling air-ICP for Be, Cr, and Pb are listed in Table 1. Cadmium and Hg were not detected using the air-ICP system during the testing at DIAL, so no values are tabulated for these metals. As discussed in this report, the detection limits for Cd and Hg during the testing at DIAL were poorer than laboratory-determined air-ICP values, and higher than the RM-29 measured aerosol concentrations for these metals. For Be, Cr, and Pb, two values are listed in Table 1 for RM-29, run 1. The “calibration spiking” column lists the values obtained for the time-scan monitoring and calibration spiking experiments performed after the RM-29 sampling, described in Section 3.2 of this report (Figures 7 and 8). The “RM-29 sampling” column of air-ICP values lists the metal aerosol concentrations for the time-scan monitoring performed during the RM-29 sampling period, calculated using the calibration curves obtained from the spiking experiments. The air-ICP aerosol concentrations listed in Table 1 were calculated using measured values for the ultrasonic nebulizer efficiency and gas flow rate through the Teflon sampling chamber, obtained after the air-ICP testing at DIAL, rather than the estimated values given in Section 3.2. The difference in the measured and estimated nebulizer efficiency (14.2% and 15%, respectively), is offset by the difference in the calculated and measured sampling chamber gas flow rates (22 and 20.75 L/min). As a result, the air-ICP aerosol concentrations listed in Table 1 are the same as those given in Section 3.2. No air-ICP concentrations for Be, Cr, and Pb are listed in Table 1 for the second RM-29 sampling period. These three metals were detected using the continuous sampling air-ICP system during the second RM-29 run on September 16 at levels comparable to the values measured during run 1, but no calibration spiking experiments were performed during or after this sampling period. In addition, a change in the optical alignment of the 0.2-m monochromator – echelle spectrometer was made at the beginning of RM-29 run 2, so the calibration curves for Be, Cr, and Pb obtained for run 1 are not valid for run 2.

For Be, Cr, and Pb, higher air-ICP signal intensities were measured during the RM-29 sampling period than those measured later, during the calibration spiking experiments that were done. Therefore, the RM-29 air-ICP determined aerosol concentrations listed in Table 1 are higher (73, 63, and 56 $\mu\text{g/dscm}$ for Be, Cr, and Pb) than the calibration spiking values (52, 57, and 44 $\mu\text{g/dscm}$, respectively). The reason for this difference is not known. It may be due to a variation in the operation of the nebulizer used to introduce metal aerosols into the stack, but there may also be other possible reasons for the differences observed. The sampling probe used for the RM-29 sampling was removed from the stack after RM-29 run 1, prior to the air-ICP calibration spiking experiments that were done. This may have caused differences in the stack gas flow patterns in the vicinity of the air-ICP probe for the calibration spiking experiments compared to the RM-29 sampling time period. After the RM-29 probe was removed from the stack, the Roots blower speed was reduced slightly to re-establish the same gas flow rate into the axial channel of the ICP torch (0.3” of water differential pressure indicated on the oil-filled manometer) that was used during the RM-29 sampling period. As discussed in Section 3.2, if calibration spiking experiments had been performed during and after the RM-29 sampling (rather than only after the sampling period), more insight into the likely reasons for the differences between the calibration spiking and RM-29 air-ICP results would have been obtained. The accuracy of the air-ICP determined aerosol concentrations compared to the RM-29 results is also listed in Table 1. For Be and Cr, the air-ICP concentrations determined during the RM-29 sampling period are about 5% higher than the RM-29 results; for Pb, the air-ICP determined concentration is less accurate, 20% lower than the RM-29 value. The reason for the poorer accuracy for Pb, compared to that for Be and Cr, is not known. The calibration spiking air-ICP aerosol concentrations for Be, Cr, and Pb, determined after the RM-29 sampling period, are about 5-40% lower than the RM-29 results.

Table 1. Analysis Results for RM-29 Sampling and the Continuous Sampling Air-ICP CEM at DIAL.

	RM-29 Results (?g/dscm)		
	Run 1		Run 2
Beryllium	70		73
Cadmium	75		87
Chromium	60		63
Lead	70		74
Mercury	66		-
	Continuous Sampling Air-ICP Values (?g/dscm)		
	Run 1		Run 2
	RM-29 Sampling	Calibration spiking	
Beryllium	73	52	-
Cadmium	-	-	-
Chromium	63	57	-
Lead	56	44	-
Mercury	-	-	-
	Difference (%)		
	Run 1		Run 2
	RM-29 Sampling	Calibration spiking	
Beryllium	(+) 4.3	(-) 25.7	-
Cadmium	-	-	-
Chromium	(+) 5.0	(-) 5.0	-
Lead	(-) 20.0	(-) 37.1	-
Mercury	-	-	-